Analysis of Condensation Polymerization Reactors. I. Kinetic Model

T. T. SZABO and J. F. LEATHRUM,* *Plastics Division, Union Carbide Corporation, Bound Brook, New Jersey*

Synopsis

A mathematical model for the kinetics of polycondensation reactions was developed. Reaction rates were expressed in terms of reactive functional groups where the reactivity of each functional group was assumed to be independent of the size of the polymer molecule. A method of testing the validity of the model with batch reactor data is demonstrated. The model is then employed to derive expressions for the equilibrium constant and molecular weight distributions. Continuous reactor yields and molecular weight distributions are then predicted from the batch reactor data. The reactions considered include chain growth, scission, and ester exchange reactions.

INTRODUCTION

The molecular weight distribution of both vinyl and condensation polymeric systems may be greatly influenced by the manufacturing method for the polymer. For instance, a polymer prepared by a batch method may not result in the same distribution as one prepared in a continuous stirred vessel reactor. Since the physical properties of polymeric systems can change with variations in molecular weight distributions, it was essential that a method be developed to predict the molecular weight distributions obtained with various processing techniques.

Traditionally, condensation polymerization has been treated as a random chain growth and scission process. Probability theory has been employed to predict molecular weight distributions, and extensive experimental evidence has been reported by Flory which supports the results of probability theory.[1] The theory was also developed to a very complete form by Case.[2] The probability approach to molecular weight distribution offers no information about the time required for the polymerization. This information is essential for a complete analysis of batch reactions and is indispensable in the design of continuous reactors on the basis of batch reactor data.

Because of the shortcomings of probability theory outlined above, it was necessary that a new model for polycondensation reactions be sought. Any new model would be required to give the same results as probability

* Present address: Department of Statistics and Computer Science, University of Delaware, Newark, Delaware.

theory plus additional information concerning the time of reaction. This paper describes one such model which was developed from absolute reaction rate theory. It should be emphasized that the model to be developed in this paper is justified only by its use in reactor design. The model is completely consistent with the Flory theory and offers no advantage over the Flory approach for the analysis of equilibrium processes.

This work is divided into three parts. In Part I the kinetic model for polycondensation reactions will be derived. Part II will then employ the kinetic model in the analysis of batch reactors, and Part III will use the kinetic model and the results of batch experiments to predict molecular weight distributions for continuous reactors.

DISCUSSION

The kinetic analysis of polycondensation reactions is complicated by the very large number of molecular species participating in the reactions. The analysis is greatly simplified, however, by Flory's[1] equal reactivity model. In this model the rates of polymerization, degradation, and interchange are independent of the chain length of the reacting molecules. Flory employed this model to predict molecular weight distributions in batch polymerizations. Case[2] refined the model to include nonstoichiometric initial conditions.

In this paper the implications of the equal reactivity model will be discussed in the following areas: (1) the choice of a theoretically reasonable expression for the equilibrium constant; (2) the transient behavior of measurable chemical variables in batch reactors; (3) molecular weight distributions in continuous flow stirred tank reactors.

Rather than resort to probability theory as Flory did, the equal reactivity model will be developed in terms of deterministic rate expressions. This will require careful choice of the important reactive species. The monomers will be designated by A-A and B-B. The important reacting species will be the A and B endgroups of which there are two on each molecule. The A and B endgroups react to produce a middle group, M, a volatile byproduct, ϕ.

$$A_i + B_j \underset{k_r}{\overset{k_f}{\rightleftharpoons}} M + \phi \tag{1}$$
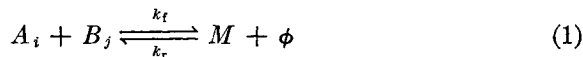
where A_i = A endgroup with i monomers in the chain B_j = B endgroup with j monomers in the chain. The rate constants, k_f and k_r, are assumed to be independent of the length of the chain to which the endgroups are attached.

The Kinetic Model

The rate expressions for the forward and reverse reactions may now be assumed to include all the pertinent bimolecular reactions. Each reaction will be second order. The forward and reverse reaction rates will now be

TABLE I
Reactive Functional Groups in the Polymer Chain

Number of monomers in the chain		
1	A_1A_1	B_1B_1
2	$A_2M_{12}{}^A B_2$	
3	$A_3M_{13}{}^A M_{23}{}^A A_3$	$B_3M_{13}{}^{BB} M_{23}{}^{BB} B_3$
4	$A_4M_{14}{}^A M_{24}{}^A M_{34}{}^A B_4$	
5	$A_5M_{15}{}^A M_{25}{}^A M_{35}{}^A M_{45}{}^A A_5$	$B_5M_{15}{}^{BB} M_{25}{}^{BB} M_{35}{}^{BB} M_{45}{}^{BB} B_5$

considered separately. In writing the rate expressions for each functional group, the change of concentration, due to both the chemical reaction of the functional group and the change of subscript when the other end of the molecule reacts, must be accounted for. Table I defines the subscripts used here.

Forward reaction.

$$dA_1/dt = - 2k_f A_1 \sum_{n=1}^{\infty} B_n$$

$$dA_2/dt = k_f A_1 B_1 - k_f A_2 \sum_{n=1}^{\infty} B_n - k_f B_2 \sum_{n=1}^{\infty} A_n$$

$$dA_3/dt = 2k_f A_1 B_2 - 2k_f A_3 \sum_{n=1}^{\infty} B_n$$

$$dA_4/dt = k_f A_1 B_3 + k_f A_2 B_2 + k_f A_3 B_1 - k_f A_4 \sum_{n=1}^{\infty} B_n - k_f B_4 \sum_{n=1}^{\infty} A_n$$

where A_i is the concentration of A endgroups with i monomers in the chain, B_j is the concentration of B endgroups with j monomers in the chain, and k_r is the forward specific rate constant.

Table I, which shows the location of functional groups, is given as a ready reference for the derivations which follow.

It should be noted that because of symmetry in the molecules with n odd, that some of the middle groups are equivalent.

$$M_{i,n}{}^A = M_{n-i,n}{}^A$$

$$M_{i,n}{}^{BB} = M_{n-i,n}{}^{BB}$$

If the concentrations of these groups could be measured, the measured value would be two times the individual concentrations. This is because the two ends of the molecule are indistinguishable.

By careful accounting of each endgroup it is found that the sum of these rate expressions becomes

$$\frac{d}{dt}\left(\sum_{n=1}^{\infty} A_n\right) = - k_f \left(\sum_{n=1}^{\infty} A_n\right)\left(\sum_{n=1}^{\infty} B_n\right) \tag{2}$$

Reverse reaction.

$$dA_1/dt = 2k_r\phi \sum_{n=2}^{\infty} M_{1n}{}^A + 2k_r\phi \sum_{n=2}^{\infty} M_{2(n-1),\,2n-1}{}^A$$

$$dA_2/dt = - k_r\phi M_{12}{}^A + k_r\phi \sum_{n=3}^{\infty} M_{2n}{}^A + k_r\phi \sum_{n=3}^{\infty} M_{n-2,\,n}{}^A$$

$$+ k_r\phi \sum_{n=3}^{\infty} M_{2,\,2n-3}{}^{BB} + k_r\phi \sum_{n=3}^{\infty} M_{2n-5,\,2n-3}{}^{BB}$$

$$dA_3/dt = - 2k_r\phi M_{13}{}^A - 2k_r\phi M_{23} + 2k_r\phi \sum_{n=4}^{\infty} M_{3n}{}^A + 2k_r\phi \sum_{n=4}^{\infty} M_{2(n-3),\,2n-3}{}^A$$

$$\cdot$$
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$$\cdot$$

where $M_{ij}{}^A$ is the concentration of the ith middle group in a chain of j monomers counting from the A endgroup, $M_{ij}{}^{BB}$ is the concentration of the ith middle group in a chain of j monomers with B endgroups on both ends of the chain, and k_r is the reverse specific rate constant.

Now the sum of all these reaction rates becomes

$$\frac{d}{dt} \sum_{n=1}^{\infty} A_n = k_r\phi M \tag{3}$$

where M is the sum of all the middle group concentrations and ϕ is the concentration of volatile by-product.

The algebraic sum of all these forward and reverse rate expressions gives the overall reaction rate

$$dA/dt = - k_f AB + k_r\phi M \tag{4}$$

where

$$A = \sum_{n=1}^{\infty} A_n$$

$$B = \sum_{n=1}^{\infty} B_n$$

The equal reactivity model does not in itself lead one to expect such a simple rate expression as eq. (4). The simplicity of this expression arises

from the choice of the reacting species as different from the molecular species.

The Equilibrium Constant

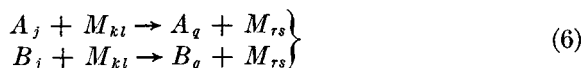Equation (4) leads to the following logical definition of the equilibrium constant

$$K = k_f/k_r = \phi M/AB \tag{5}$$

where in a real solution A, B, M are concentrations of ϕ is an activity.

Flory derived a similar rate expression from considerations of statistical mechanics.[3] He showed that the only activity that needs to be considered is that of the by-product. The activity of the by-product must be evaluated from vapor–liquid equilibrium data. The thermodynamic consistency of the equal reactivity model has been proven by Flory's work, however.
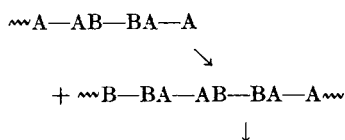
Ester Exchange Reactions

Ester exchange reactions include the following:

$$\left.\begin{array}{c} A_j + M_{kl} \to A_q + M_{rs} \\ B_j + M_{kl} \to B_q + M_{rs} \end{array}\right\} \tag{6}$$

$$M_{ij} + M_{kl} \to M_{pq} + M_{rs} \tag{7}$$

where $j + l = q + s$ in each case, and $A_i = $ A endgroup with i structural units in the chain, $B_j = $ B endgroup with i structural units in the chain, and $M_{ij} = i$ the middle group in a chain of j structural units. In these ester exchange reactions the numbers of each functional group and molecules remains the same. It is possible to reason from this observation alone that eq. (4) remains valid. This conclusion will be used later to test the validity of the rate expressions for ester exchange. In more practical terms, by definition ester exchange reactions do not change the degree of polymerization. These reactions will alter the molecular weight distribution of any product which is not at its "most probable distribution" as defined by Case[1] and Flory.[3] In other words, while ester exchange is occurring, holding the degree of polymerization constant, the number-average molecular weight also remains constant, but the weight-average molecular weight is changing until the most probable distribution is reached.
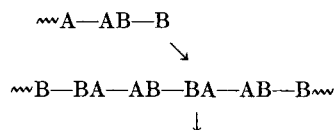
Ester exchange reactions may be summarized as follows.
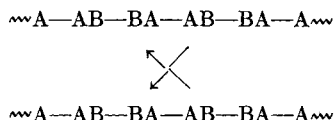
A + M ester exchange:

$$\sim\!\!A\text{—AB—BA—A}$$
$$\searrow$$
$$+ \sim\!\!B\text{—BA—AB—BA—A}\sim$$
$$\downarrow$$

where BA or AB are middle groups, M, A and B are endgroups.

B + M ester exchange:

$$\text{\scriptsize\textasciitilde}A—AB—B$$

$$\searrow$$

$$\text{\scriptsize\textasciitilde}B—BA—AB—BA—AB—B\text{\scriptsize\textasciitilde}$$

$$\downarrow$$

M + M ester exchange

$$\text{\scriptsize\textasciitilde}A—AB—BA—AB—BA—A\text{\scriptsize\textasciitilde}$$

$$\times$$

$$\text{\scriptsize\textasciitilde}A—AB—BA—AB—BA—A\text{\scriptsize\textasciitilde}$$

The arrows indicate the new bonds formed and new endgroups which result.

The contributions of ester exchange to the specific rate expressions may now be written by assuming second-order reactions.

$$dA_1/dt = -2k_3A_1M + 2k_3A \sum_{n=2}^{\infty} M_{1n}{}^{A} + 2k_3A \sum_{n=1}^{\infty} M_{2n,2n+1}{}^{A}$$

$$dA_2/dt = -k_3A_2M - k_3AM_{12}{}^{A} + k_3A \sum_{n=2}^{\infty} M_{2n-2,2n}{}^{A} + k_3A \sum_{n=1}^{\infty} M_{2,2n+1}{}^{BB}$$

$$+ k_3A \sum_{n=1}^{\infty} M_{2n-1,2n+1}{}^{BB} + k_3A_1\left(\sum_{n=1}^{\infty} M_{n-1,2n}{}^{A} + \sum_{n=1}^{\infty} M_{1,2n+1}{}^{BB} + \sum_{n=1}^{\infty} M_{2n,2n}{}^{BB} \right).$$

$$dA_3/dt = -2k_3A_3M - 2k_3A(M_{13}{}^{A} + M_{23}{}^{A})$$

$$+ 2k_3A\left(\sum_{n=4}^{\infty} M_{3n}{}^{A} + \sum_{n=2}^{\infty} M_{2n-2,2n+1}{}^{A} \right) + 2k_3A_1\left(\sum_{n=3}^{\infty} M_{2n}{}^{A} + \sum_{n=2}^{\infty} M_{2n-1,2n+1}{}^{A} \right)$$

$$dA_4/dt = -k_3A_4M - k_3A(M_{14}{}^{A} + M_{24}{}^{A} + M_{34}{}^{A})$$

$$+ k_3A\left(\sum_{n=3}^{\infty} M_{2n-4,2n}{}^{A} + \sum_{n=2}^{\infty} M_{4,2n+1}{}^{BB} + \sum_{n=2}^{\infty} M_{2n-3,2n+1}{}^{BB} \right)$$

$$+ k_3A_1\left(\sum_{n=2}^{\infty} M_{2n-3,2n}{}^{A} + \sum_{n=2}^{\infty} M_{3,2n+1}{}^{BB} + \sum_{n=2}^{\infty} M_{2n-2,2n+1}{}^{BB} \right)$$

$$+ k_3A_2\left(\sum_{n=3}^{\infty} M_{2n}{}^{A} + \sum_{n=1}^{\infty} M_{2n-1,2n+1}{}^{A} \right)$$

$$+ k_2A_3\left(\sum_{n=1}^{\infty} M_{2n-1,2n}{}^{A} + \sum_{n=1}^{\infty} M_{1,2n+1}{}^{BB} + \sum_{n=1}^{\infty} M_{2n,2n+1}{}^{BB} \right)$$

By summing the rate expressions with careful accounting for the functional groups it is found that

$$\frac{d}{dt}\left(\sum_{n=1}^{\infty} A_n \right) = 0 \tag{8}$$

where k_3 is the specific rate constant for A + M ester exchange. The A + M ester exchange also changes the concentrations of the B-type endgroups.
For $n = 1$,

$$dB_1/dt = 0$$

For n even,

$$\frac{dB_n}{dt} = \frac{dA_n}{dt}$$

For n odd, $\neq 1$,

$$\frac{dB_n}{dt} = - 2k_3A \sum_{i=1}^{n-1} M_{i,n}{}^{BB} + 2k_3 \sum_{j=1}^{n-1/2} A_{2j}$$

$$\times \left(\sum_{s=j}^{\infty} M_{2s+2j-n,2s}{}^{A} + \sum_{s=j}^{\infty} M_{2s-n+2j+1,2s+1}{}^{BB} \sum_{s=j}^{\infty} M_{n-2j,2s+1}{}^{BB} \right)$$

Once again it may be shown that

$$\frac{d}{dt} \left(\sum_{n=1}^{\infty} B_n \right) = 0 \tag{9}$$

By a very similar procedure the rate expressions for B + M and M + M ester exchanges may be derived. In each rate expression it is possible to express the middle group concentrations in terms of endgroup concentrations (for the method see the Appendix).

CONCLUSIONS

By a proper choice of reacting species, reaction rate expressions for condensation polymerization were derived with the following convenient features: (1) equal reactivity concept was incorporated and fully utilized; (2) a very simple overall rate expression is obtained by summation; (3) the reaction equilibrium state corresponds to a thermodynamic equilibrium state; (4) all possible bimolecular reactions between the reacting species could be incorporated in the model.

These features now make it possible to devise experiments to validate the kinetic model and to derive design equation for commercial reactors.

APPENDIX

Derivation of Rate Expressions for Ester Exchange Reactions

The rate expressions for B + M and M + M ester exchange will be derived here. In each case one must consider all those reactions which will change the number of moles of the functional group of interest.

B + M Ester Exchange.   Consider first the rate of change of B_1

$$dB_1/dt = -2k_4B_1M + 2k_4B \sum_{n=1}^{\infty} M_{1,2n+1}^{BB}$$

$$+ 2k_4 \sum_{n=1}^{\infty} M_{2n,2n+1}^{BB} + 2k_4B \sum_{n=1}^{\infty} M_{2n-1,2n} \quad (A-1)$$

or

$dB_1/dt = $ change of B_1 due to reaction of B_1 with any M

+ change of B_1 due to reaction of any B with a middle

group in the first position from any B endgroup.

Similarly, for B_2,

$$dB_2/dt = -k_4B_2M - k_4BM_{12}^A + k_4B\left(\sum_{n=3}^{\infty} M_{2,n}^A + \sum_{n} M_{2n-1,2n+1}^A\right)$$

$$+ k_4B_1\left(\sum_{n=2}^{\infty} M_{1,n}^A + \sum_{n=1}^{\infty} M_{2n,2n+1}\right) \quad (A-2)$$

or

$dB_2/dt = $ change of B_2 due to reaction of B_2 with any M + any B
with M_{12}^A + any B with a middle group in the second position
from an A type endgroup + B_1 with any middle group in the
first position from any A type endgroup.

In like manner, the rate expressions for B_3, B_4 etc. may be written as follows.

$$dB_3/dt = -2k_4B_4M - 2k_4B(M_{13}^{BB} + M_{23}^{BB})$$

$$+ 2k_4B\left(\sum_{n=2}^{\infty} M_{2n-3,2n}^A + \sum_{n=2}^{\infty} M_{3,2n+1}^{BB} + \sum_{n=2}^{\infty} M_{2n-2,2n+1}^{BB}\right)$$

$$+ 2k_4B_1\left(\sum_{n=2}^{\infty} M_{2n-2,2n}^A + \sum_{n=1}^{\infty} M_{2,2n+1}^{BB} + \sum_{n=1}^{\infty} M_{2n-1,2n+1}^{BB}\right) \quad (A-3)$$

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The B + M ester exchange reaction also affects the concentration of A_1
endgroups:

$$dA_1/dt = 0 \quad (A-4)$$

i.e., there is no way that B and M can react to produce A_1.

$$dA_2/dt = dB_2/dt. \quad (A-5)$$

A_2 and B_2 are on the same molecule.

For an odd number of structural units (i.e., n odd),

$$dA_n/dt = -k_4 B \sum_{i=1}^{n-1} M_{i,n}{}^A + 2k_4 \sum_{j=1}^{n-1/2} B_{2j}$$

$$\times \left(\sum_{s=2j}^{\infty} M_{n-2j,s}{}^A + \sum_{s=j}^{\infty} M_{2s+2j-n+1,2s+1} \right) \quad \text{(A-6)}$$

or,

dA_n/dt = change of A_n (n is odd) due to reaction of
B with a middle group in the A_n molecule + B_i
with any middle group in the $(n-i)$ position from an
A-type endgroup (i even).

M + M ester exchange.   For M + M ester exchange,

$$dA_1/dt = dB_1/dt = 0 \quad \text{(A-7)}$$

i.e., there is no way in which two middle groups can react to produce a monomer molecule.

$$dA_2/dt = -k_5 M M_{12}{}^A + k_5 \left(\sum_{n=1}^{\infty} M_{1n}{}^A + \sum_{n=1}^{\infty} M_{2n,2n+1}{}^A \right)$$

$$\times \left(\sum_{n=1}^{\infty} M_{1,2n+1}{}^{BB} + \sum_{n=1}^{\infty} M_{2n,2n+1}{}^{BB} \right) \quad \text{(A-8)}$$

Thus,

dA_2/dt = change of A_2 due to reaction of any M with $M_{12}{}^A$ + any M in the
first position for an A endgroup with any M in the first position
from a B endgroup.

$$dA_3/dt = -2k_5 M(M_{13}{}^A + M_{23}{}^A) + 2k_5 \left(\sum_{n=1}^{\infty} M_{1,n}{}^A + \sum_{n=1}^{\infty} M_{2n,2n+1}{}^A \right)$$

$$\times \left(\sum_{n=1}^{\infty} M_{2,n}{}^A + \sum_{n=1}^{\infty} M_{2n-1,2n+1}{}^A \right) \quad \text{(A-9)}$$

For the B-type endgroups,

$$dB_2/dt = dA_2/dt \quad \text{(A-10)}$$

$$dB_n/dt = dA_n/dt \quad \text{For even } n \quad \text{(A-11)}$$

$$dB_3/dt = -2k_5 M(M_{13}{}^{BB} + M_{23}{}^{BB})$$

$$+ 2k_5 \left(\sum_{n=1}^{\infty} M_{2n-1,2n}{}^A + \sum_{n=1}^{\infty} M_{1,2n+1}{}^{BB} + \sum_{n=1}^{\infty} M_{2n,2n+1}{}^{BB} \right)$$

$$\times \left(\sum_{n=2}^{\infty} M_{2n-2,n2}{}^A + \sum_{n=1}^{\infty} M_{2,2n+1}{}^{BB} + \sum_{n=1}^{\infty} M_{2n-1,2n+1}{}^{BB} \right) \quad \text{(A-12)}$$

References

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953.

2. L. C. Case, *J. Polym. Sci.*, **29**, 455 (1958).

3. P. J. Flory, *J. Chem. Phys.*, **12**, 425 (1944).